TIRUVENKATA RAJENDRA SESHADRI

(1900–1975)

Elected F.N.I. 1942

Birth, Parentage and Early Life

Thiruvenkata Rajendra Seshadri was born on February 3, 1900 to Thiruvengadatha Iyengar and Namagiri Ammal at Kulitalai, situated on the bank of river Kaveri in Tiruchy district of Tamil Nadu in South India. Seshadri's father was a teacher in a local school and the family was known for its piety. Seshadri was the third of the five sons. He went to the National College High School in Tiruchy city, founded by men imbued with high patriotic fervour. Life in this school naturally left a deep impression all its alumni.

Higher Education

In India

In 1917, Seshadri moved to the metropolitan city of Madras and joined the Presidency College, a seat of higher learning founded by the British. There he came under the influence of some very inspiring teachers of Chemistry; he carried fond memories of his teacher, Professor P. A. Narayana Iyer. Cost of living in large metropolitan cities was high even in those days and even with the merit scholarship Seshadri received, his college education became a financial strain on his family. He, therefore, had to look for relief and this came from the Ramakrishna Mission, which admitted Seshadri to its Students' Home. The association with the Ramakrishna Mission was to have a lasting effect on Seshadri. The discipline in the Students' Home, the simple living and high thinking practised there, the dedication, sense of duty and the spiritual atmosphere prevailing there, shaped Seshadri's life in a manner no other institution could have done. Seshadri remained adherent to ideals of the Ramakrishna Mission throughout his life.

After receiving the Honours degree in Chemistry of the University of Madras, Seshadri worked with the Ramakrishna Mission for one year, helping in the organisation in their new Residential High School. Later, he joined the Chemistry Department of the Presidency College, Madras, as a University Research Scholar, under the guidance of its head, (the late) Professor B. B. Dey. For his work which was partly on Indian medicinal plants and partly on coumarins, the University of Madras awarded him two prizes, the Sir William Wedderburn Prize and the Curzon Prize.

T. R. Seshadri

AT MANCHESTER, LONDON, GRAZ, EDINBURGH : 1927–30

In 1927, Seshadri secured an overseas technical scholarship from the Government of Madras and sailed to England to work at the University of Manchester under the celebrated Professor Robert Robinson (F.R.S.) who was attracting research workers from all over the world. Seshadri's Ph.D. thesis consisted of two parts : (1) Search for new antimalarials and (2) Synthesis of anthocyanins. Seshadri cherished his association with Robinson School as the most important event in his scientific career and felt that through this he had become a member of the great Perkin family of Organic Chemists. Seshadri's personal loyalty to Professor Robinson was very intense and unswerving, and it was fully and generously reciprocated by his great master, who considered Seshadri among his most outstanding pupils. In his message on the 60th birthday of Seshadri (1960) printed in the special souvenir volume, Professor Robinson wrote :

> "*Even if Professor Seshadri were known to me only as an author of original memoirs in the Chemical Journals, I would be gratified to have this opportunity to add my tribute to his fertility of ideas, his technical skill in execution and his qualities of energetic drive and wise planning. His original researches have indeed given him worldwide recognition and he is unsurpassed in the experimental survey of the groups of natural products on which he has concentrated his attention. But to me, he is no mere name in the literature; I have enjoyed the inestimable privilege of following his development almost from the beginning. His work in my laboratory, especially on the synthesis of anthocyanins, was of the highest calibre and went far to encourage us to pursue the attack in this difficult region of synthesis. It is not appropriate here to recount the outstanding achievements to the credit of Seshadri and his school; that is the purpose for which this volume is dedicated. Suffice it to say that we do homage to a most sincere scientist of unassailable integrity, a brilliant and devoted teacher and a most generous friend.*"

After receiving the Ph. D. degree of the University of Manchester and before returning to India, Seshadri worked for brief periods in other important centres in Europe. He spent some months in Graz in Austria learning organic microanalysis in the laboratory of Professor Fritz Pregl, the father of quantitative organic micro-analysis. This new technique reduced the quantity of organic substances required for analysis by a factor of nearly 20, and this contributed to the rapid progress in the chemistry of natural products in the decades that followed. It was for this significant contribution to organic chemistry that Professor Pregl was awarded the Nobel Prize, in 1923. Another laboratory where Seshadri worked for about eight months was that of Professor George Barger, F.R.S. who then occupied the Chair of Medical Chemistry at the University of Edinburgh. Here he was associated with work on the chemistry of retrorsine. This substance falls under the group of quinolizidine alkaloids, which received their full elucidation years later, and Seshadri contributed to the chemistry of this group in the mid sixties. Seshadri also spent a short period in the laboratory of Mr Cameron, Chief Agricultural

Analyst to the country of Fife, where he acquainted himself with methods of agricultural chemistry.

Coimbatore and Andhra University : The War Years

At the conclusion of his foreign training, Seshadri returned to India in 1930. The country was caught in the worst economic depression the world had seen; in addition, it was rocked by national struggle for freedom from British rule. Career openings were rare for qualified scientists. Seshadri chose to become a Research Fellow in the University of Madras and after some months joined a Government Research post in the Agricultural College and Research Institute at Coimbatore as a soil analyst. Although this institution afforded him opportunities to become acquainted with different aspects of agricultural science, particularly plant chemistry and plant protection, there was little scope for fundamental work. When three years later an opportunity arose, Seshadri joined the Andhra University at Waltair, as Senior Lecturer and Head of the new Chemistry Department. This called for a great deal of organisational work. Laboratories had to be built and equipped and courses of studies had to be framed. Starting from scratch, Seshadri built up a fine Department of a progressive university. While his laboratories were yet under construction, Seshadri used to rush on a bicycle to the Biochemistry Department of the Andhra Medical College at Visakhapatnam, three miles away, to do his own research. In 1934, Seshadri was appointed Reader and in 1937 Professor of Chemistry in the University. His zeal and dedication for research were so infective that a number of young men joined him. In 1937, he was also given the responsibility of looking after the University Department of Chemical Technology. The financial resources of the two departments were small by present-day standars, but by very prudent husbanding, they served to sustain the activities of a number of workers. 1937 was also the year when Seshadri laid the beginnings of the Department of Pharmaceutical Sciences of the Andhra University.

The laboratories that Professor Seshadri was building were beginning to take shape when the Second World War broke out (1939) and supplies of chemicals and scientific goods from Europe, on which educational institutions in India had largely to depend, became scarce. In 1941, came other restrictions, and laboratory work had to be curtailed. Towards the close of the academic year 1941–42, the harbour at Visakhapatnam, situated about 4 miles away from the University campus, was bombed by the Japanese. This necessitated the evacuation of the entire town of Visakhapatnam including Waltair and the University campus. The University buildings were commandeered by the Defence Department and the laboratories so laboriously built up over the years were dismantled and transformed into a military base hospital. All the University teaching departments and administrative offices were moved to a relatively safe inland location, Guntur, about 300 miles south, and accommodated in whatever buildings could be acquired on rent and in hastily put up temporary sheds. This was hardly satisfactory and the Chemistry Department of the Andhra University was shifted to Madras at the beginning of the academic year 1943–44. Class work was done in the Chemistry Department of the Presidency College and the Biochemical Research Laboratories of the University of Madras.

With this change, the setback to research experienced by the Chemistry Department during 1942–43 was partly overcome and work began to pick up once more. Even with all the restrictions imposed by the state of war, a remarkably large volume of research work was turned out and several young people were able to obtain their doctoral degrees.

The year 1945 saw the formal end of hostilities, and all the departments of the Andhra University moved back to Waltair at the commencement of the academic year 1946–47. However, the Chemistry laboratories had to be re-built, since they had been completely dismantled. The task of reconstruction was not easy as there was shortage of almost every item in the post-war years. The stoppage of scientific supplies from Europe that began at the commencement of the War turned out to be a permanent feature and the tardiness in the development of a fine chemical industry in the country plagued Indian Science for at least a decade after the War. Professor Seshadri's enthusiasm for research, however, never flagged and it is to the eternal credit of this undaunted and dedicated scientist that he continued to produce high class work in these manifestly adverse circumstances.

University of Delhi and the Advanced Centre for the Chemistry of Natural Products

Resettlement at Waltair was only just complete when Professor Seshadri had to face a moral crisis. The University of Delhi had formally been established in 1925 but had yet no teaching department of its own. The early forties saw some growth but it was only after Sir Maurice Gwyer become its Vice-Chancellor that real progress began. In 1949, he took a major decision to organise post-graduate teaching and research in the sciences. To achieve this, he looked for the best talent available in the country. Sir Maurice invited Professor Seshadri to head the Chemistry Department. It was not easy to leave the Andhra University where Seshadri had built up an active school of teaching and research. Also, Delhi University did not seem a propitious place initially. However, after weeks of indecision, Seshadri finally agreed to join the Delhi University in July 1949.

It did not take Professor Seshadri long to transform the Department into one of the most active centres in the country for research on the Chemistry of Natural Products. In this mission, he received support not only from Sir Maurice Gwyer but also his successors. In 1957–58, he received a gift of the much needed instruments like UV and IR spectrometers from USA under the Wheat Loan grants. These instruments had by then become indispensable aids and their availability stepped up the pace of research. The best equipment, however, was really the human material. A large number of intelligent and highly motivated young students joined him. To them Professor Seshadri set the pattern not only for Chemistry but also for dedication and other human values. The laboratories were kept open from early morning till late in the night and Professor Seshadri was always there to guide, advise and help. It was common knowledge that Professor Seshadri had no home or social life; he was always in the laboratory. Sustained work by competent and dedicated students led to a flow of high quality publications which appeared in the foremost of Indian and foreign scientific journals. The fifties were so productive that in 1960,

he received the high distinction of being elected Fellow of the Royal Society of London. That was also the year when he completed sixty years of age and his election was a fitting recognition of two decades of hard work.

In 1962, the University Grants Commission (UGC) selected Seshadri's Department as the Centre for Advanced study in the Chemistry of Natural Products in India and made him its first Director. It was with the organisation of this Advanced Centre that the author of this memoir was invited to join the Delhi University group. The Centre attained great distinction in the Chemistry of Natural Products ever since it came into existence.

Active Research In the Post-Retirement Years : 1965–75

In 1965, Professor Seshadri completed sixty five years of age and according to the rules of the University, he retired from all formal administrative positions and responsibilities in the Chemistry Department. The University, however, appointed him as its first-ever Emeritus Professor, thereby providing him with the possibility of continuing his researches. Many science funding agencies of the country such as the Council of Scientific and Industrial Research (CSIR), the Indian Council of Medical Research (ICMR), the Indian Council of Agricultural Research (ICAR) and the Indian National Science Academy entrusted him with important research projects. The U.S. Department of Agriculture also funded projects through their PL-480 programmes. These brought him adequate funds and support for a number of young scholars. Being freed of the administrative responsibilities, Seshadri could devote all his time to research.

Professor Seshadri suffered a massive heart attack in January 1965 which incapacitated him considerably, and, from which he recovered sufficiently to be able to carry on his work, though not with the same vigour as before. His dedication to chemistry was so great that in the post-retirement years the research publications practically doubled, with the result that when he died in 1975, he had around 1200 publications and had trained more than 150 Ph.Ds.

Professor Seshadri desired that young men and women should become good research scientists and in this he met with great success. Many who worked with him in the fifties are now leaders of research not only in India but also in several foreign countries. To mention only a few, Pofessors P. S. Rao, L. R. Row, K. Neelakantam, V. V. S. Murti, S. K. Mukerjee, A. C. Jain, S. Neelakantan, G. B. V. Subramanian V. K. Ahluwalia, Dr Varadarajan and Dr K. Aghoramurthy. The author of this memoir wrote with Professor Seshadri a book entitled, *Chemistry of Vitamins and Hormones* whose first edition appeared in 1946 and the second in 1952.

Professor Seshadri firmly believed that science alone cannot solve the problems of Man. His faith in moral and spiritual education was deep and abiding. Along with Swami Ranganathananda, then Chief of the Delhi Unit of the Ramakrishna Mission, he started the Delhi University Vedanta Samiti, which held regular Sunday morning meetings at which spiritual matters were discussed with the help of ancient texts of India and explained in terms of modern scientific concepts. Professor Seshadri strongly believed that the academic community had a special and unique responsibility to society, and that mere academic achievements divorced

from ethical, moral and spiritual moorings were a danger. He encouraged his students to participate in the activities of this study group.

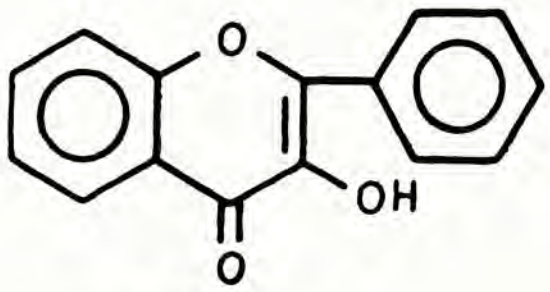
Service to Science in the National Sphere

Professor Seshadri's rich experience as a chemist and scientist was utilised by the scientific community and the Government of India in several ways. He was chairman or member of expert bodies of several Universities. He was member of the Pharmacy Council of India, Ministry of Health, Governing Body of Indian Council of Medical Research (ICMR) and Chairman of its Expert Committee on Indigenous Drugs. He was Chairman of the Chemical Research Council of the Council of Scientific and Industrial Research (CSIR), a member of its Governing Body, Chairman of the Executive Council of the Regional Research Laboratory, Jammu, Member of the Executive Council of the National Chemical Laboratory, Poona, and of the Regional Research Laboratory, Hyderabad (all under the CSIR). He was Chairman of several expert committees of ICMR, CSIR and the Indian Council of Agricultural Research (ICAR), the University Grants Commission (UGC) and the Ministry of Education and Scientific Research, the Ministry of Health, Ministry of Agriculture, Ministry of Defence and the Department of Atomic energy of the Government of India. He was Chairman of Review Committee of the Indian Institute of Science, Bangalore and of the Indian Lac Research Institute, Ranchi. He was a member of several committees for selection of candidates for foreign scholarships. He was a member of the Scientific Advisory Committee to the Cabinet and of the Committee on Science and Technology of the Government of India. For sometime, he was a consultant to the UNESCO.

Contributions to Scientific Knowledge

Oxygen Heterocyclics

Professor Seshadri, whose major contributions have been in the area of oxygen heterocyclics, began with the isolation and structure elucidation of the flavonoid pigments of Indian plants, both aglucones and glucosides, and developed methods of methylation to facilitate the degradative study of the aglucones to get an insight into the structure of the glucosides. For providing synthetic support to the structures of new members which have a higher degree of oxygenation, methods had to be evolved for introducing more hydroxyl groups into various positions. The converse procedure for removal of hydroxyl groups was also worked out. Methods of partial methylation and demethylation were also evolved as part of the strategy. These studies were extended from flavones and flavonols to insoflavones, flavanones, chalkones, aurones, isoflavanones, dihydroflavonols, xanthones and anthraquinones involving plant materials of various families and genera. Methods of total synthesis and interconversions in these areas were also elaborated. Further sophistication arose in many cases of natural compounds by the presence of C-methyl groups, C-prenyl groups, furan rings, chromene rings and combinations of these and methods were evolved for their study by classical and modern methods and synthesis.



FLAVONOL

The flavandiols called leucoanthocyanidins by Professor Seshadri had eluded isolation and study for decades. These and the catechins which are related to anthocyanidins and tannins are optically active and their chemistry and stereochemistry received considerable attention by the Seshadri Group.

Coumarins, halocoumarins, 3-phenyl-and 4-phenyl-coumarins and groups of natural compounds related to them also engaged the attention of the Seshadri school. Other groups of compounds derived from flavonoids or coumarins and characterised by the presence of an additional ring resulting from an oxide bridge connecting the pyrone ring and the side phenyl ring, bi-flavonoids and flavanolignans, which are of rather restricted natural occurrence, were additional areas of his research.

Professor Seshadri showed deep concern with the problems of his country and this led to his involvement with the rational utilisation of natural resources like medicinal plants, poisonous plants, dyestuff plants, insecticidal plants and other economic plants of the country like *Psoralea corylifolia, Pongamia glabra,* species of *Dalbergia, Pterocarpus, Acacia, Morinda, Albizzia, Gossypium, Cassia, Citrus* and *Pinus.*

Professor Seshadri was the pioneer Indian chemist who made an extensive chemical study of the lichens of India and their chemical components, involving degradation and synthesis.

After compiling a vast volume of data, it was a natural step to trace their evolution and propose theories of biogenesis. Professor Seshadri has propounded biogenetic theories on practically all the groups of compounds which came to his attention.

Methylation of Anthoxanthins and Glycosides

Sustained fundamental research by Professor Seshadri commenced at the laboratories of the Andhra University, Waltair, during the mid-thirties concerned the examination of the brightly coloured flowers of several species of cotton (*Gossypium*) plants (family Malvaceae). The studies were later enlarged to cover other genera of the Malvaceae, like *Hibiscus.* This belongs to compositae and *Thespesia.* A large number of individual compounds of the anthoxanthin group were isolated both as free aglycones and as glycosides. The aglycones were studied by the classical methods that had been developed in western laboratories involving alkaline degradation, oxidation etc; initially the free aglycones themselves were degraded, but later, it was found to be more advantageous to degrade the methyl ethers, since this enabled easier isolation and recognition of the degradation fragments. Methods of methylation, therefore, became important and assumed

even greater importance for the investigation of glycosides to locate the position of the sugar residue.

Earlier methods for methylation of anthoxanthins and their glycosides were not quite satisfactory. Methyl iodide is too volatile and costly, diazomethane is not only poisonous but does not succeed well with chelated hydroxyl groups. Seshadri developed the method of using dimethyl sulphate and anhydrous potassium carbonate in boiling acetone medium, which helped in achieving complete methylation of all phenolic hydroxyl groups including the chelated one at the 5th position. For ethylation, ethyl iodide or di-ethyl sulphate along with potassium carbonate was used. When it is necessary to retain the 5-OH free for further transformation, the above dimethyl sulphate/potassium carbonate method is obviously unsuitable. The study of gossypin, the 8-glucoside of gossypetin, provides a good example wherein these techniques have been employed.

During the last two decades or more, the recognition of the existence of free hydroxyl groups in flavonoids in different positions and indeed the recognition of the type of flavonoid itself have been largely systematised on the basis of UV-visible spectral study employing neutral solvents, followed by addition of traces of various reagents like sodium acetate, sodium methoxide, aluminium chloride, borax, etc. They have been regularly employed in the studies of the Seshadri school.

Oxidative and Selective Demethylation

Oxidative demethylation has been developed by the Seshadri school as an elegant synthetic tool in connection with the structure of many natural substances, e.g., gossypin and the quino-chalkones of *Didymocarpus pedicellata,* and has been extended to substances not easily accessible otherwise e.g., carthamidin and norkhellin.

Nuclear Oxidation and Reduction

The development of synthetic methods for nuclear oxidation and reduction was a natural corollary to the isolation of a large number of anthoxanthins with varying oxygenation patterns. These were needed to provide synthetic support to structures deduced from degradative studies and also to enable acceptance or rejection of theories of biogenesis of flavonoids and related compounds based initially on speculation. Professor Seshadri and his school developed two distinct methods for introducing a hydroxyl *para* or *ortho* to an existing hydroxyl. Such introduction has been possible both in simple aromatic structures, in flavonoid precursors (chalkones) and in the finished flavonoid structures. Potassium persulphate in a strongly alkaline medium was employed for introducing a para hydroxyl.

Introduction of a hydroxyl into the *ortho* position was effected in two stages; first a formyl was introduced into the *o*-position by heating with hexamine in glacial acetic acid (Duff reaction) or by the Gattermann reaction (in a few cases an acetyl was introduced by *o*-acetylation followed by Fries migration); the formyl (or acetyl) was subsequently replaced by hydroxyl by heating with alkaline hydrogen peroxide (Dakin oxidation). These methods found extensive application not only in the laboratories of Profesor Seshadri but in many other laboratories in the world studying oxygen heterocyclics.

Nuclear reduction in Professor Seshadri's laboratory has been achieved in ring A and in the side phenyl ring of anthoxanthins by selective tosylation of the hydroxyl to be reduced and hydrogenolysis of the tosyester. The reduction is achieved in the following order of positions : 7, 5, 3′ 4′. Nuclear reduction has been implicated in the biogenesis of several members of the flavonoid group of compounds.

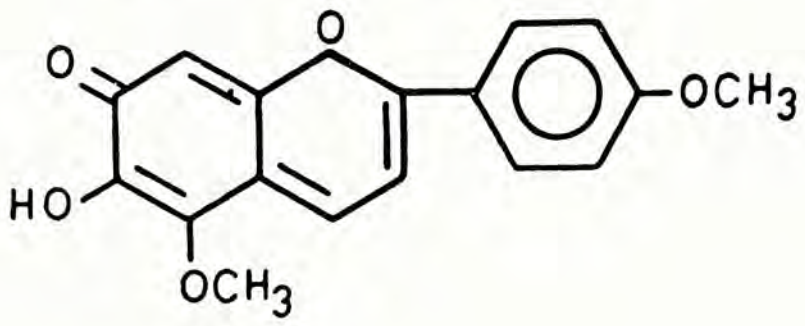
Anthocyanins, Leucoanthocyanidins and Qninonoid Anhydro Bases

Part of Seshadri's Ph.D work at Manchester was on the synthesis of anthocyanins. Of the four possible glucosides of pelargonidin chloride, the 3-glucoside (calistephin) had been synthesised earlier by Robertsonand Robinson* andSeshadri synthesised the remaining three. In the fifties, an intensive survey of anthocyanins was carried out at the Delhi University laboratories covering the flowers of many garden plants, avenue trees, forest trees and many edible fruits and agricultural cash crops. But the major thrust of the Seshadri school was in the area of leucoanthocyanidins (or pro-anthocyanidins as Professor Freudenberg would call them, with greater justification). Methods were evolved for getting good yields of anthocyanidins from other polyphenols. Intensely coloured compounds related to the leuco base of anthocyanidins and called quinonoid anhydro bases which had eluded precise understanding for decades also came under the scrutiny of the Seshadri school.

For the survey of anthocyanins, Seshadri and his coworkers employed the methods devised originally by Professor Robinson, like colour reactions and other qualitative tests, supplemented by new techniques that had come up like paper chromatography and absorption spectral studies.

Work in the area of leucoanthocyanidine has been difficult; even the isolation is tricky and crystallisation succeeds reasonably well only under fortuitous circumstances. When the pseudobase of a 7-hydroxy-flavylium salt i.e., 2,7-dihydroxy-flav-3-ene, undergoes loss of the elements of water involving the hydrogen of the 7-OH (leaving as H^+) and the OH at the 2-position (leaving as OH^-), a quinone methide structure result, in which the quinonoid conjugation extends to position 3 : 2, and into the side phenyl nucleus, resulting in deep colour. This is referred to as quinonoid anhydro base or quinone base. Compounds of this type are rather difficult to obtain crystalline. Two important natural quinonoid anhydro bases which have been obtained crystalline are carajurin and carajurone present in the cosmetic used by South American natives and called carajura (chica red) prepared from the plant *Bignonia chica*. In crystalline form carajurin is garnet red and carajurone scarlet red. They are related to the flavone scutellarein (4′, 5′, 6, 7-tetrahydroxyflavone). The pseudo base of the corresponding anthocyanidin scutellareinidin, when it loses the elements of water in the aforesaid manner, yields the red quinone base carajuretin (4′, 5, 6-trihydroxy-7-quinonoid base) which can also be obtained by demethylation of the natural substances carajurone which is its 4′-O-methyl ether or carajurin which is its 4′, 5-di-O-methyl ether. Professor Robinson had assigned the correct structure of carajurin as early as 1927, and Professor Seshadri provided synthetic support for it in the 1950's. 2, 4, 5-Trihydroxy-6-methoxybenzaldehyde (prepared by the para oxidation of 6-0-methyl-phloroglucinaldehyde) when condensed with

*Robertson, A., and Robinson, R. (1928) *J. chem. Soc.*, 1460.

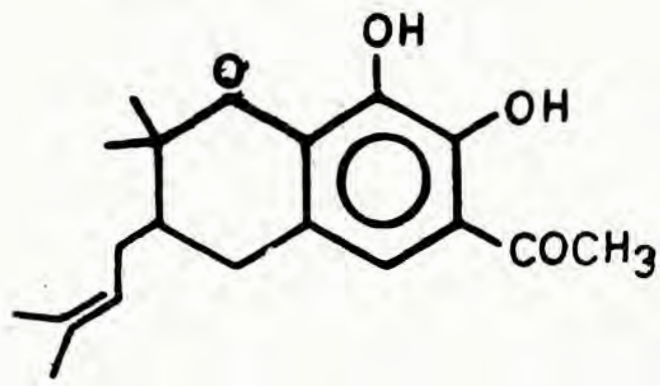


CARAJURIN

4-methoxyacetophenone and hydrogen chloride yielded carajuridin chloride (6 7 dihydroxy-5,4′-dimethoxy-flavylium chloride), treatment of which with sodium acetate yielded the anhydro base carajurin. Carajurin can be reconverted into the flavylium salt carajuridin chloride by the action of HCl.

Nuclear Methylation, Allylation and Prenylation

A large number of C-methylated benzopyrones have been discovered in nature, and to establish their identity synthetic C-methyl reference substances were needed. The early nuclear methylation studies began even in the late thirties and were extended during the subsequent two decades. Nuclear prenylated compounds both as such and in cyclised forms were discovered in abundance in nature during the sixties and this area of research stimulated Professor Seshadri's nuclear prenylation studies. These studies covered flavones, flavonols, chalkones, flavonones, isoflavones, xanthones and coumarins. Since 7-hydroxy-flavanones and -coumarins can undergo ring opening in the presence of base, they behave like resacetophenone. Where the pyrone ring is stable to alkali, the 7-hydroxy compounds fail to give the C-methyl derivative. Invariably some *o*-methyl derivatives are simultaneously produced. 5,7-dihydroxy-benzo-pyrones give the 6-C-methyl derivatives as expected. (Where direct C-methylation fails as with 7-hydroxy-flavone, a two-step method has been used with success, by introducing a formyl at position 8 using the Duff reaction and then reducing the formyl to methyl by catalytic hydrogenation. But this cannot be considered as real C-methylation). By such methods the following C-methyl compounds, among others, have been synthesised like for example , eugenitin, iso-eugenitin, iso-eugenitol, pino-querectin, angustifolionol and strobochrysin. C-prenylation has been studied extensively in the late sixties and early seventies. γγ-Dimethyl allyl bromide which gives *o*-prenyl derivatives with potassium carbonate in refluxing acetone, gives the C-prenyl derivatives in addition when the reaction is carried out in the presence of methanolic sodium methoxide, and only the C-prenyl compound with butyl lithium in benzene. 2-Methyl-but-3-en-2-ol in the presence of boron trifluoride-etherate has been extensively used to achieve C-prenylation. C-prenylation has been very successfully achieved with suitably substituted aromatic compounds, benzo-α-pyrones and benzo-γ-pyrones. Prenylation could be simultaneously achieved both in the benzene ring and side phenyl ring in flavonoids and occasionally two prenyls entered the same position, the nucleus reacting in the diketo form. The initial *o*-hydroxy-prenyl derivative could be cyclised using acidic reagents to yield a 2′-isopropyl-dihydrofuran or a 2′ 2′-dimethyl-dihydropyran, which on subsequent



dehydrogenation with DDQ gives the isopropyl furan or a dimethyl-pyran. A unique reaction was noticed with gallacetophenone. The first Pr unit entered the 5-position as expected, but it attracted a second prenyl at its 2′-position and simultaneously itself underwent cyclisation to dimethylchroman, the resulting product being 2, 2-dimethyl-3-prenyl-6-acetyl-7, 8-dihydroxy-benzochroman.

Studies on the Wesseley-Moser Rearrangement

Rearrangement of 5, 8-hydroxyflavones to the 5, 6-isomers and of 5, 7, 8-trihydroxy flavones to 5, 6, 7-isomers during attempted demethylation of the methyl ethers by boiling with hydriodic acid, has been known as the Wesseley-Moser rearrangement. Professor Seshadri and his coworkers made extensive studies with different oxygen heterocyclics which led to an understanding of the structural features influencing the change and to the synthesis, among others, of muningin and hinokiflavone.

2′-Benzyloxy chalkones give the epoxides by the action of alkaline hydrogen peroxide. When subjected to the action of acidic reagents like boron tri-fluoride-etherate or etheral hydrogen chloride these epoxides give different products depending on the substituents in the two aromatic rings and the experimental conditions. Two of the major products are the dihydroflavonol and the α-formyl deoxybenzoin which on cyclisation gave the isoflavone.

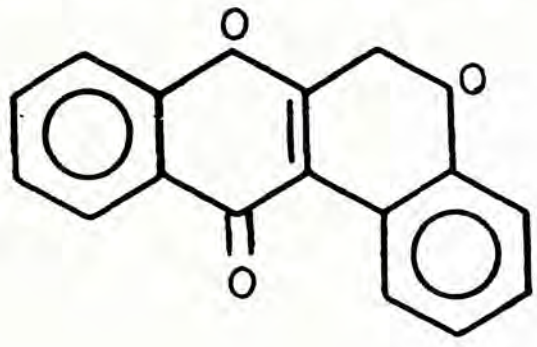
Synthesis of Furano-Chromones, Chromeno-Chromones, Chromeno-Flavones, etc.

Furano-chromone, chromeno-flavone and furano-chromeno-chromone are structures present in many substances having physiological activity. The earliest substance in this group that came to the attention of Seshadri was Karanjin isolated from the seed oil of *Pongamia glabra*. The structure of this substance had been established as 3-methoxy-furano (2′, 3′, 7, 8)-flavone by Professor Spath. In connection with its synthesis, Seshadri developed methods for construction of a furan ring on to chromones, flavones, coumarine etc. and conversely of an α- or γ-pyrone ring on to a benzofuran.

Further, similar method was followed for the synthesis of the linear furano-chromone khellin (the active principle of *Ammi visnaga*) which is 2-methyl-5, 8-dimethoxy-furano (2′ 3′ 7′, 6)-chromone. Starting from 2-methyl-5, 7-dihydroxy-chromone, the 7-0-acetic ester was prepared, another hydroxyl was introduced into the 8-position by *p*-oxidation, and a formyl group into the 6-position. Cyclisation of

the 5,8-dimethyl ether with acetic anhydride/sodium acetate was accompanied by decarboxylation and yielded khellin.

The isolation of several α, α-dimethylchromenes from natural sources led to synthetic attempts in this field. An aromatic hydroxyl is converted into the 1,1-dimethyl propargyl ether by heating with 3-chloro (or bromo) 3-methyl-but-1-yne in acetone solution with anhydrous potassium carbonate and in the presence of potassium iodide. The propargyl ether side chain cyclises to the α, α-dimethyl-chromene on heating in a high boiling solvent like dimethylaniline. In the flavonoid field, in general, the angular isomers are the major products and linear isomers the minor. In rare cases spontaneous cyclisation takes place, at least partially, even during the formation of the ether. In an alternative route, the propargyl ether was partially hydrogenated, ring closed by the action of acidic reagents to give a pyran ring and then dehydrogenated with DDQ to get the α, α-dimethylchromenes.



CHROMENO (3′,4′:2,3)-
CHROMONE

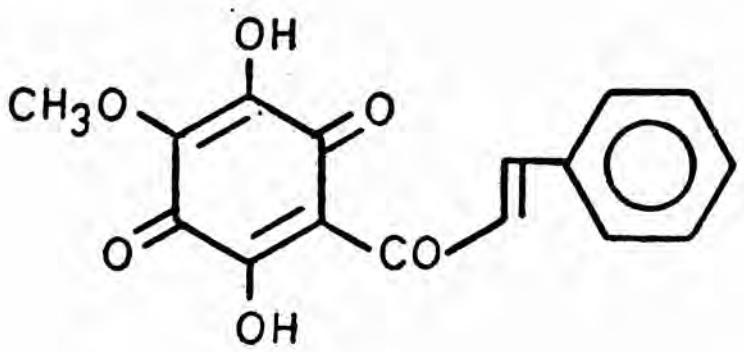
For the synthesis of the chromeno-(3′ 4′ : 2, 3)-chromone ring as is found in members of the rotenoid group, Professor Seshadri made a biogenetic approach. The highly characteristic chromeno ring was considered to be the result of dehydration between the CH_2OH group at position 2 and the OH at position 2′ of the side phenyl in a 2-hydroxymethyl-2′-hydroxy-isoflavone. A 2′-hydroxyl or methoxyl was provided, according to the circumstances of the case, either (*a*) by starting with an *o*-hydroxy or methoxy-benzoic acid or acetophenone prior to pyrone ring closure, or (*b*) by introducing the 2′ -OH in the finished flavone by *p*-oxidation. Providing the CH_2OH group at the 2-position was slightly more involved. Attempts were first made to convert the reactive CH_3 group at position 2 into CH_2OH. This was achieved by the action of N-bromosuccinimide (in the presence of benzoyl peroxide) on the acetate of the parent compound. The bromine was then replaced by OH by boiling with dilute, hydrochloric acid. Elimination of water between the 2-CH_2OH and 2′-OH groups was easily achieved by boiling an acetone soluttion of the compound with anhydrous potassium carbonate. The product was the required chromeno-chromone.

Study of Some Indian Medicinal Plants

Butea frondosa– This Indian medicinal plant has been the subject of investigation in several laboratories. Perkin isolated the aglycone butin (7, 3′, 4′-trihydroxy-flavanone). Lal and Dutt isolated a glycoside called butrin which they considered to

contain two glucose units present as a biose attached to the aglucone. Seshadri and coworkers established the correct structure of butrin as 7,3′-di-*o*-glucosylbutin. They also isolated and established the structure of the chalkone corresponding to the free aglycone, viz.,3, 4, 2′, 4′-tetra-hydroxy-chalkone called butein (1) and the 3, 4′-di-*o*-glucoside of butein called isobutrin. A coumarone glycoside called palasitrin also from the same plant source was shown to be 2-(3-glucosyloxy-4-hydroxy benzylidine)-6-glucosyloxy-coumaran-3-one. It was thus related to isobutrin having the sugars in the same position but it was a benzylidene coumaranone instead of a chalkone. It was, therefore, an easy step to convert isobutrin into palasitrin. This was effected by acetylating isobutrin, making its dibromide and treating it with alcoholic potash whereby ring closure to coumaranone and deacetylation took place yielding palasitrin.

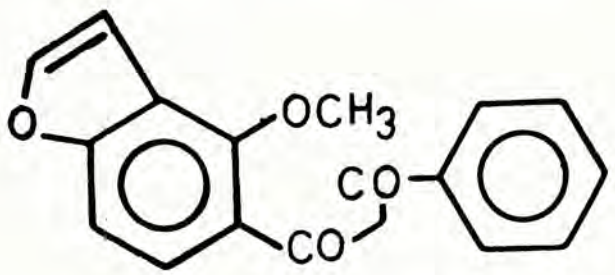
Didymocarpus pedicellata—From the leaves of this medicinal plants Siddiqui first isolated pedicellin which was shown to be 2′,3′,4′,5′,6′-pentamethoxy chalkone. The structure proposed by Siddiqui for the dihydroxy-trimethoxy chalkone pedicine was revised by Seshadri to 2′,5′-dihydroxy-3′,4′,6′-trimethoxy chalkone. Usual ring closure of this chalkone yielded the flavanone called isopedicine (6-hydroxy-5, 7,8-trimethoxy-flavanone). Mild oxidation of pedicine with benzoquinone or silver oxide yielded the 2′ 6′-quinone(quinochalkone). Of the three methoxyls (at 3′,4′ and 6′-positions) in this quinochalkone those at 3′ and 6′ positions could be hydrolysed to hydroxyl by mild treatment with sodium hydroxide yielding the dihydroxy mono-methoxy-quinochalkone, pedicinin, while only the methoxyl at 6′ position was hydrolysed with sodium bicarbonate yielding the monohydroxy- dimethoxy-quinochalkone, methylpedicinin.



PEDICININ

While on the topic of *D. pedicellata* it may be mentioned that a succinic acid derivation has also been isolated from the leaves and named pedicellic acid. Its structure has been established as 2-methyl-3-tridecyl-succinic acid.

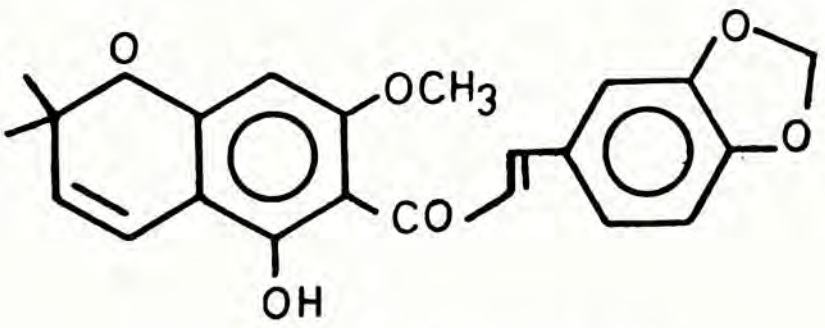
Carthamus tinctorius—The flowers of this plant were examined by Professor Perkin as early as 1918. Seshadri provided new methods for the synthesis of the aglycone carthamidin (5′,7′,8′,4′-tetrahydroxy-flavanone) and its isomer isocarthamidin (5,6,7,4′-tetrahydroxy-flavanone). The yellow substance called carthamin was shown to be 4,3′,4′,6′-tetrahydroxy 2′-glucosyloxy-chalkone, the red principle carthamone to be the corresponding 3′, 6′-quinochalkone with the glucosyloxy and other hydroxyls in the same position and another colourless accompanying substance neo-carthamin to be the corresponding flavanone viz. 5-glucosyloxy-6,7,4′-trihydroxy-flavanone.



PONGAMOL

Prunus puddum — The first natural isoflavanone to be isolated by Seshadri & coworkers was padmakastein (5,4′-di-hydroxy-7-methoxy-isoflavanone) from the bark of *Prunus puddum*, together with padmakastin which is its glucoside. Padmakastein derivatives are dehydrogenated with SeO_2 to prunetin isoflavone) derivatives and the converse is achieved by hydrogenation in the presence of palladium carbon.

Pongamia glabra—This is an important plant in Indian folk medicine. From its seed oil, a substance called karanjin was isolated and its structure established by Professor Spath as 3-methoxy-furano-(2′,3′,7,8) flavone in the 1930's. Later investigations have all come from Seshadri's laboratories. Other components isolated from the seed are kanjone (6-methoxy-furano-(2′,3′,7,8)-flavone), pongapin (3-methoxy-3′,4′-methyl-enedioxy-furano-(2″,3″,7,8)-flavone) and the corresponding 3-demethoxy compound called ponga-glabrone and a β-diketone called pongamol (1-2-methoxy furano-(2′,3′,$_5$4,3)-phenyl-3-phenyl propane-1,3, dione). The roots and stem bark contained kanugin (3,7,5′-trimethoxy 3′,4′-methylenedioxy flavone), demethoxykanugin(the 5′-demethoxy compound) and pongachromene a chromenoflavone (3-methoxy-3′, 4′-methylenedioxy 6″, 6″ dimethylpyrano-(2″,3″,7,8)-flavone). The leaves contain the chromeno-chalkone called glabrachromene which is 2,2-dimethyl-5-hydroxy-7-methoxy-chrom-3-ene with a 3,4-methylenedioxycinnamoyl residue at position 6. A minor compound recently isolated from the leaves is 3′-methoxypongapin.



GLABRACHROMENE

A compound belonging to an entirely different chemical group which was obtained also from the seeds is glabrin. Its structure remined unresolved for three decades until high resolution mass spectrometry led to its structure as 4,5-dihydroxy-N-methyl-piperidine-2-carboxylic acid.

Psoralea corylifolia—The seeds of this plant constitute a well-known drug in Indian medicine. Its active principles, psoralen and isopsoralen (angelicin) were studied by Professor Spath in the thirties and shown to be linear (7,6) and

angular (7,8) furocoumarin respectively. A revival of interest in this drug during the fifties led to new methods of synthesis and to the isolation of new substances from it. Following a biogenetic pathway, 6-C-prenyl- or 6-allyl-7-hydroxy-coumarin was ozonolysed by Seshadri and coworkers and the resulting 6-acetaldehyde ring-closed (PPA has been found to be a very good condensing agent) to give psoralen. Isopsoralen (angelicin) was similarly synthesised from the 8-allyl-7-hydroxy coumarin. New compounds isolated from the drug are bavachin (6-prenyl-7,4'-dihydroxy-flavanone) and isobavachin(its 8-prenyl isomer), the chalkone(4,2',4'-trihydroxy-5'-prenyl-chalkone) corresponding to bavachin called bavanchalkone, and the analogous isobavachalkone (3'-prenyl compound). They have all been synthesised. When the prenyl residue in bavach*al*kone closes up the ring with the hydroxyl ortho to it, it results in the chalkone α,α-dimethylchroman which can be dehydrogenated to the chromene which also occurs in the seed and has been named bavachromene. A new isoflavone called neobava-isoflavone has also been isolated from the seeds and shown to be 3'-prenyl-7,4'-dihydroxy-isoflavone.

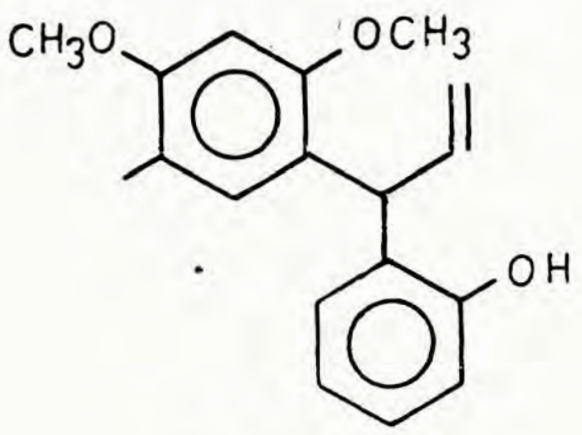
Gossypol—Gossypol, the golden yellow colouring matter of cotton seed and its oil have been studied in the USA, India and USSR. The gross structure of the molecule was established by Professor Roger Adams of USA as a symmetrically substituted 2,2'-binaphthyl with hydroxyls at 1,6 and 7 positions, formyl at 8, a methyl at 3 and an isopropyl at 5, in each half of the molecule. Seshadri worked out a convenient method for obtaining gossypol from cotton seed oil be precipitating the sparingly soluble anil and heating it with acetic anhydride whereby gossypol hexacetate is obtained. Confirmatory evidence for the *o*-hydroxy-aldehyde grouping in gossypol was provided by Seshadri by utilising this structural feature to build up α-pyrones and flavylium salts.

During his work relating to Gossypol, Professor Adams had observed that Gossypol and its derivatives like the hexamethyl ether and the hexa-acetate did not show constant melting point or crystal form. This is due to the fact that the hydroxyl at 1 and the formyl at 8 position in gossypol can ring-close to form a lactol and this can happen in one or both rings. Further, at each lactol carbon, two configurations are possible. Professor Seshadri succeeded in isolating all the six methyl ethers and two acetates in pure form.

Another important aspect of gossypol studies is the optical activity of the parent substance and its derivatives. Much light on this was shed by the study of gossypol isolated from *Thespasia populnea*, another plant of the family Malvaceae. Professor Seshadri prepared apo ad des-apo gossypol in optically active forms from (+) gossypol, proving thereby the presence of atropo-isomerism in gossypol and its derivatives.

Neoflavonoids

The term neoflavonoids was introduced into the literature during the sixties to denote 4-phenylcoumarins and related compounds which comprise mainly the following groups : dalbergins, dalbergiquinols, dalbergiquinones, 4-phenyl-3-chromenes and brazilins (4-phenylchromans with a methylene bridge connecting position 3 and 2'). Professor Seshadri has contributed much to the first four groups. The name dalbergin was given to a substance first isolated, from the heart wood of

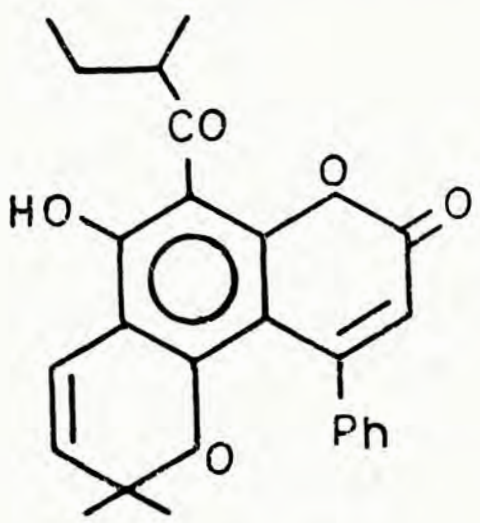


LATIFOLIN

Dalbergia sissoo and its structure was elucidated as 6-hydroxy-7-methoxy-4-phenyl-coumarin. Related compounds isolated from *D. sissoo* are the 6,7-dimethoxy-6, 7-dihydroxy- and 6-methoxy-7-hydroxy-4-phenyl-coumarins; these have been given trivial names showing their relationship to dalbergin. From *D. latifolia* a substance called latifolin was isolated whose structure was elucidated as 2,4-dimethoxy-5-hydroxyphenyl-2′-hydroxy phenyl-vinyl-methane. It can also be looked upon as a 1 : 4-quinol-1-methyl ether with a benzyl side chain in position 2 and other groups in other positions, and the parent quinol itself has been designated as a dalbergiquinol. Since it has an asymmetric carbon it is optically active and the configuration has been elucidated as R.

A compound named Dalbergichromene (6-hydroxy-7-methoxy-4-phenyl-3-chromene) has been isolated from the heart wood of *D. sissoo*. It has been synthesised by reductive ring opening of dalbergin with LAH and cyclodehydration of the resulting *o*-hydroxy-cinnamyl alcohol with acidic reagents (Amberlite IR-120 H^+ form has been found very efficient). Dalbergichromene also results from dalbergiquinone by allowing it to undergo isomerisation with hot pyridine.

Professor Seshadri has suggested a scheme for the biogenesis of these groups of compounds which is largely akin to the above laboratory methods. Union of a C6 and C9 unit, which by C-acylation gives rise to chalkone and therefrom to flavonoids



PONNALIDE

and isoflavonoids, will, by O-acylation, give rise to cinnamic esters of phenols, whose ring closure will give rise to 4-phenylcoumarins from which dalbergiquinols, dalbergiquinones and 4-phenyl-3-chromenes are easily obtainable.

A 4-phenylcoumarin obtained by Seshadri and co-workers from the tropical medicinal tree *Calophylum inophyllum* is ponnalide, which, can be represented as a 7-hydroxy-4-phenyl-coumarin with an α-methyl-butyroyl side chain at position 8 and 8 and a 2′, 2′-dimethyl-chromene ring fused to 5,6-positions constituting a chromeno-(6′5′ : 5,6)-coumarin.

Cyanomaclurin

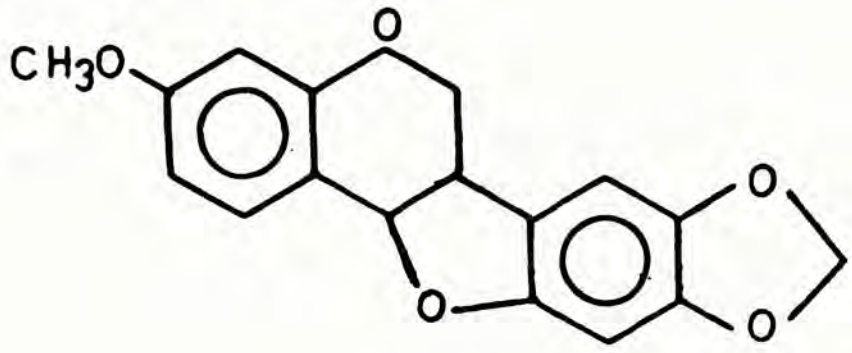
Cyanomaclurin is the chief constituent of the Indian Jack fruit tree (*Arto-carpus heterophyllus*). It was recognised long ago as a leucoanthocyanidin derivative by Professor Robinson, who gave it a hemiketal structure. The correct structure was arrived at one the basis of NMR studies by Professor Seshadri and his group and by

CYANOMACLURIN

Professor Venkataraman and his group and it is now known to be 4, 2′-oxido-3,5,7, 4′-tetrahydroxyflavan. This structure was supported by the synthesis of related structures and finally of cyanomaclurin trimethyl ether. For this 2 -benzyloxy-5,7, 4′-trimethoxyflavanone was oxidised with alkaline hydrogen peroxide to give the flavanone-3-ol. Catalytic debenzylation liberated the 2′-hydroxyl. Sodium borohydride reduced the carbonyl at 4 and under the influence of acidic reagents the 4-OH reacted with the 2′-OH eliminating water and yielded cyanomaclurin trimethyl ether.

Pterocarpans

Pterocarpans have become a sizeable group in recent decades. They have been obtained mostly from the heart woods of trees such as red sanders (*Pterocarpus santalinus*) and their structures have been deduced mainly from spectral studies. Though the first members of this group viz., pterocarpin and homopterocarpin were isolated more than a hundred years ago and their constitutions established in 1940, their synthesis had to wait till recently due to non-availability of the necessary synthetic procedures. The essential laboratory precursor is the appropriate 2′-hydroxyisoflavone. Borohydride treatment led to the reduction of the CO (position 4) to CHOH, and simultaneous reduction of the 2,3-double bond, giving isoflavan-4-ol. Treatment of the product with HCL in the course of work-up led to spontaneous



PTEROCARPIN

cyclisation involving dehydration between the hydroxyls at 4 and 2′-positions, resulting in the pterocarpan skeleton. Employing this method a number of variously substituted pterocarpans were synthesised including a racemate of homopterocarpin.

Biflavonyls

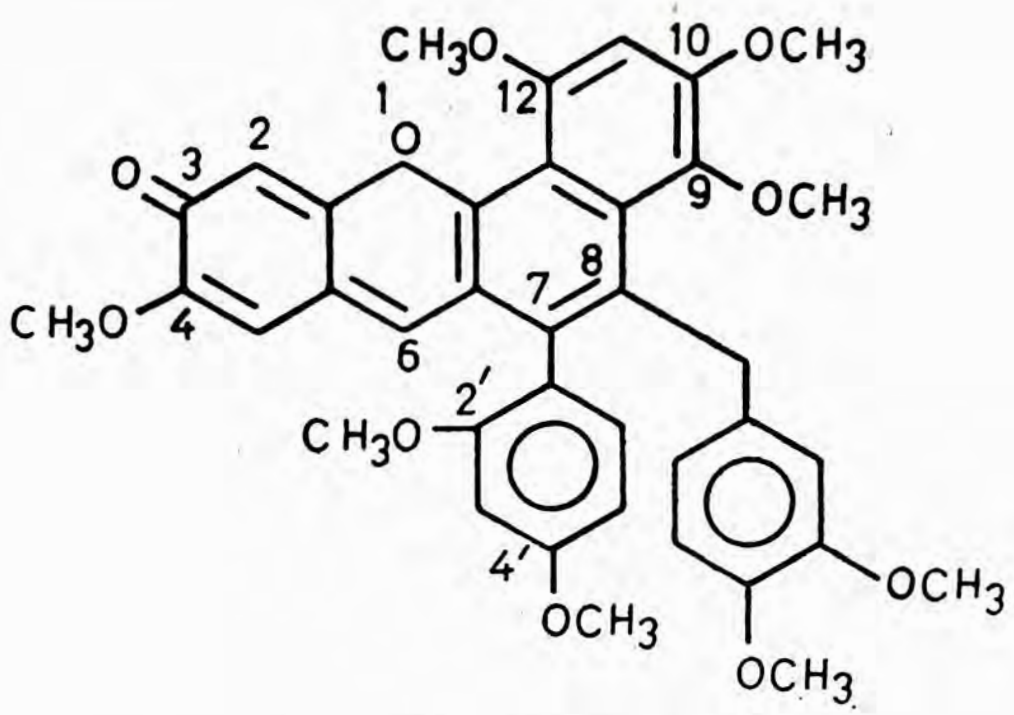
These are compounds discovered during the sixties and their structure determination is beset with several difficulties that were tackled skilfully by Seshadri and coworkers. From *Cupressus torulosa,* a compound called cupressuflavone was isolated and its structure established as a biapigeninyl. The linkage between the two flavone units could be settled satisfactorily only by approaching the problem from several angles and by comparison with model substances, synthetically prepared. For linking up the two halves of the molecule Ullmann's reaction has been the method of choice. Mass and NMR spectral methods have shed much light on the problem and cupressuflavone is now accepted to have the structure 8,8-biapigeninyl. Some other Indian plants of the Cupressaceae family have also been screened for their biflavonyl contents.

Santalin pigments

The red pigment obtained from the heart wood of the forest tree *Pterocarpus santalinus* and called santalin which formed the subject matter of early investigations in British laboratories, has now been found to be a mixture, having two major components which have been given the names santalin-A and santalin-B. Both of them have methoxyl and phenolic groups and both give the same permethyl ether, and this has been subjected to extensive degradative studies. Based on the chemical identity of the degradation products the structure of the permethyl ether, which has eight methoxy groups, has been worked out by Seshadri and coworkers. This structure is quite close to the currently accepted structure and incorporates the correct nucleus.

Bicoumarinyl

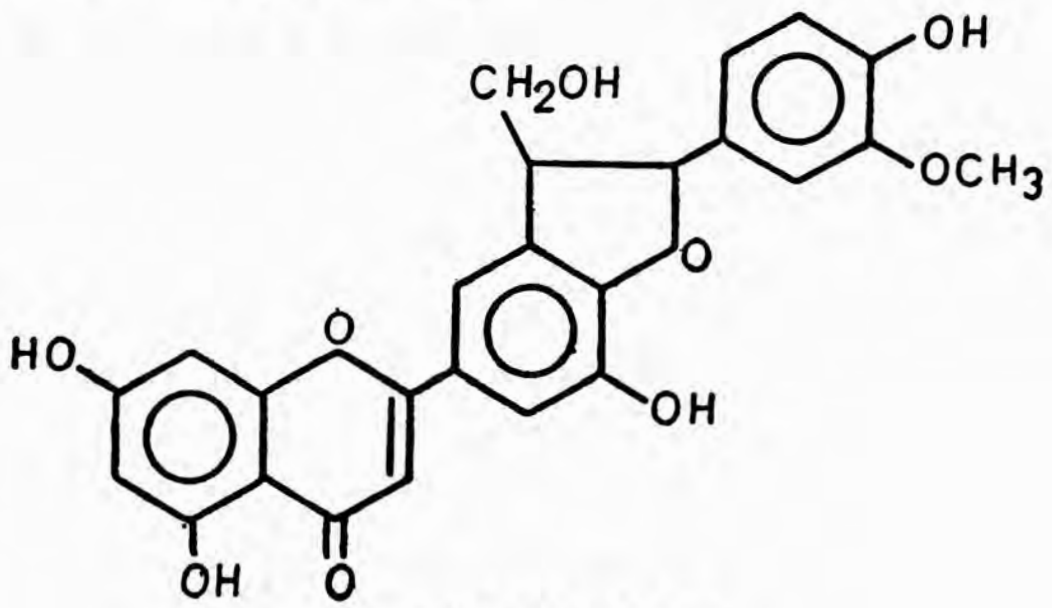
A substance designated as candicanin isolated from the roots of *Heracleum candicans* was shown to have a novel type of bicoumarimyl structure as tertiary O-imperatorinyl-heraclenol by Seshadri and his school.



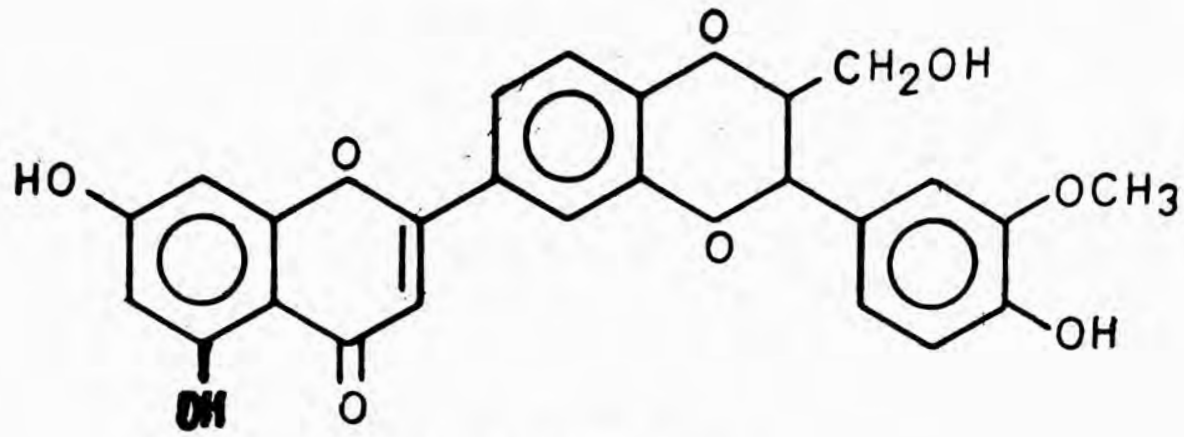
PER-O-METHYL SANTALIN

Flavonolignans

Flavonolignans are a new group of compounds consisting of a combination of a C15 (flavonoid) and C9 unit, the latter being linked to the side phenyl of the former. The first known member is silybin isolated and studied in Professor Wagner's laboratory in Munich, and is constituted from taxifolin to which the *alfa* and *beta* carbon atoms of 3-methoxy-4-hydroxy-phenyl-propanol are linked to the 4′-0 and 3′-0 respectively of taxifolin thereby constituting a new dioxane ring. From the seeds hulls of *Hydnocarpus wightiana* Seshadri and Ranganathan isolated a new substance called hydrocarpin which was studied elaborately and shown to be constituted in the same manner as silybin, with the difference that it was derived from luteolin instead of taxifolin. The same material also yielded an isomeric substance called isohydnocarpin which has a dihydrofuran rings as shown. Isohydnocarpin thus bears the same relationship to hydrocarpin that silycristin of Professor Wagner does to silybin. A third flavonolignan isolated from theseed hulls of *H. wightiana* was shown to be a methoxyhydnocarpin.



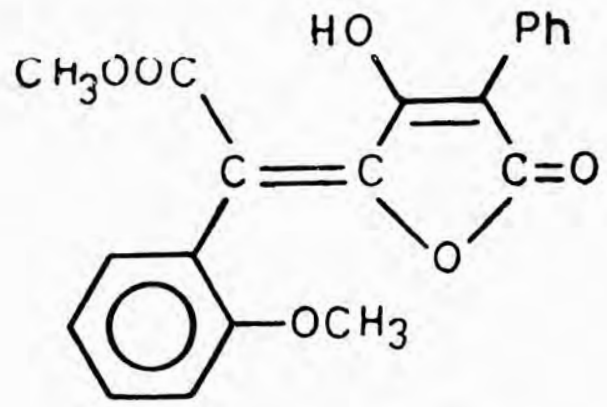
ISOHYDNOCARPIN



HYDNOCARPIN

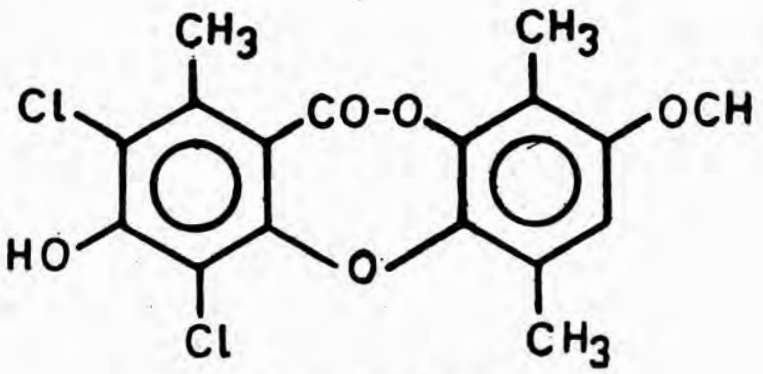
Lichen substances

Lichens are interesting plant organisms being symbionts of algae and fungi. Investigations of the components of lichens on the one hand and fungal products on the other have shown that the characteristic lichen substances are really the metabolic products of the fungi. Seshadri was a pioneer of lichen studies in India and one of the leading lichen chemists in the world. His investigations of lichens which began in the thirties when he was in the Andhra University and covered lichens growing in South India, Sri Lanka and some countries of South-east Asia were extended to lichens of the Himalayas after he moved to the Delhi University. Several new compounds were discovered, their structure established and synthesis



LEPRAPINIC ACID

effected in most cases. Mention may be made of *montagnetol, erythrin, teloschistin, virensic acid, pyxiferin, pinastric acid, leprapinic acid, vicanicin and retigeradiol.*

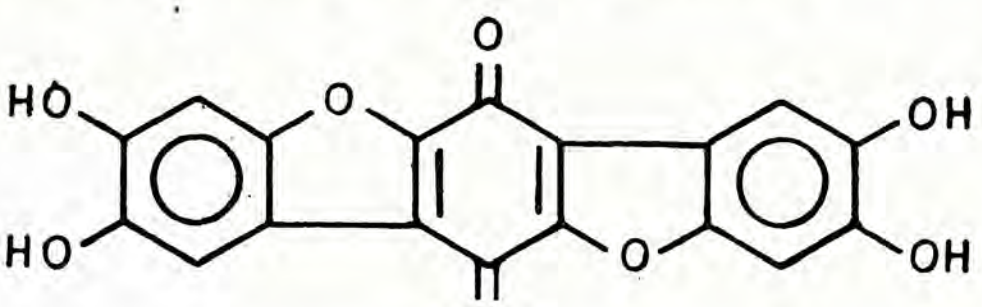


VICANICIN

C-Glycosides

The first C-glycoside to be investigated by the Seshadri school was mangiferin isolated from the mango tree (*Mangifera indica*) and some other plants. It was shown to be 2-C-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone, and it was synthesised by C-glucosylating 1,3,6,7-tetrahydroxyxanthone with tetra-acetyl-α-D-glucopyranosyl bromide, the sugar residue entering the most reactive 2-position. Two new C-glycosides isolated from the leaves of *Parkinsonia aculeata* and named parkinsonin-A and -B were shown to be β-C-glucoside of 5-0-methylluteolin with stereochemistry as in orientin and 8-C-glucoside of 5,7-di-O-methylluteolin with stereochemistry as in epi-orientin.

From *Pueraria tuberosa* the di-acetata of puerarin (8-C-β-D-glucopyranosyl-4′, 7-dihydroxy-isoflavone) was isolated. Paniculatin from the bark of *Dalbergia paniculata* was assigned the structure 6,8-di-C-glucosyl-genistein. Volubilin and iso-volubilin from the flowers of *Dalbergia volubilis* were shown to be respectively 8-C- and 6-C-L-ribopyranosyl-4′, 7-di-O-methyl-genistein. From the seeds of *Trigonella corniculata* 6,8-di-C-β-glucopyranosyl-4′-O-methyl-apigenin and its mono-acetate were obtained and their structures established.

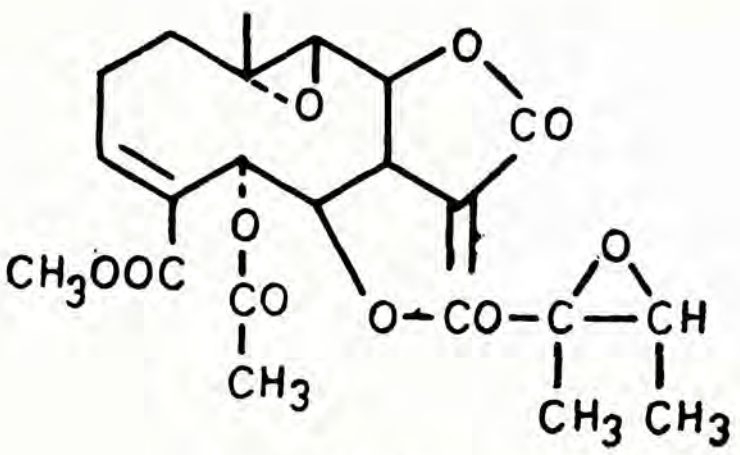


THELEPHORIC ACID

Thelephoric acid, an earlier known compound was isolated from *Labaria isidosa* and its earlier incorrect structure was corrected to that of a symmetrical terphenyl quinone. It is a 2,5-diphenyl-1, 4-benzoaquinone with an oxide bridge between 3 and 2′ and also between 6 and 2″ positions forming two furan rings, and with four free hydroxyls at 4′,5′,4″ and 5″ positions.

Terpenoids

Some amount of work an sesquiterpenes, diterpenes, triterpenes and polyterpenes was natural in the course of work on a range of natural materials. Substances of the sequiterpene group present in *Pterocarpus santalinus* have been mentioned elsewhere. Diterpenes figured in the work on *Croton oblongifolius*. Oblongifoliol and desoxyoblongifoliol have been assigned the structure entisopimara-7, 15-diene-3β, 19-diol and its 19-deoxy derivative, and the 19-carboxylic acid is oblongifolic acid. 11-Dehydrohardwickic acid is a new diterpene obtained from the same plant. (16 *alfa*-Hydroxykauran-19-oic acid was isolated from *Enhydra fluctuans* and its structure established). Enhydrin, another compound isolated from *E. fluctuans* has been shown to be a new germacranolide with two epoxy rings. Two triterpenic seco-acids, putrolic acid and putric acid and two neutral compounds putrone and



ENHYDRIN

putrol were isolated from *Putranjiva roxburghii* and their structures correlated with that of friedelin. Candicopimaric acid from *Heracleum candicans* was related to pimaric acid. Work on retigeradiol has been mentioned under lichens.

Theories of Biogenesis

The activities of the research school of Seshadri resulted in the isolation and structure study of a very large number of compounds. When the data that had thus become available were codified, it was but natural to speculate on the inter-relationships between them. Seshadri thus became interested in the possible mode of biogenesis of each group of compounds that he came across and proposed theories which were subsequently corroborated by synthetical work employing tracer techniques in his own laboratories, and in laboratories in other parts of the world.

The early speculations regarding anthoxanthins were an extension of Professor Robinson's theory of the parallel origin of the anthoxanthins from a common precursor derived from a C6 and a C9 unit, and involved ideas of sequential evolution by processes of nuclear oxidation, nuclear reduction and nuclear methylation. Schemes have also been suggested for the biogenesis of anthocyanins and of other classes of natural products like lichen depsides and depsidones, xanthones, different types of quinones like benzoquinones, naphthoquinones including binaphthyls like gossypol and perylene quinones, and anthraquinones, and mould metabolites. In all these the orsellinic acid C8 unit has been assigned a key role.

Other groups about whose origin Seshadiri speculated are naturally occurring tetronic acid derivatives, 3- and 4-phenylchromans and benzophenones' stilbenes and phenylisocoumarins, the C5 unit in plants, pulvinic acid derivatives and mould tropolones. Last came the speculations on neoflavonoids and a revised biogenesis of xanthones in Guttifearae according to which the xanthone arises from a 5-hydroxy 4-phenylcoumarin. This undergoes oxidative cyclisation between the 5-OH and 2′-position, and this is followed by ring opening and elimination of C2 and C3 of the coumarin ring. The result is a xanthone. The substitution patterns observed in natural xanthones seem to support this view of biogenesis, and the theoretical reasoning has received confirmation through laboratory synthesis.

Honours and Distinctions

The scientific community in India honoured him in several ways. He was Cooch-Behar Professor of the Indian Association for the Cultivation of Science, Calcutta, Professor H. K. Sen Lecturer of the Instiution of Chemists, India, Professor B. C. Guha Lecturer of the Indian Science Congress Association, Professor B. K. Singh Lecturer of the Panjab University and Professor K. Venkataraman Lecturer of the Bombay University. He held Honorary Professorships at the Universities of Andhra and Osmania and received the Honorary Doctorate degrees of the Universities of Andhra, Banaras, Delhi and Osmania. He was Chairman of the Indian National Committee for Chemistry and Chairman of the Panel for Chemistry and Biology under the Indo-Soviet Agreement on Scientific and Technical Cooperation. He was the leader of the Indian delegation to the First and Second Indo-Soviet Symposium on the *Chemistry of Natural Products,* held in 1968 and 1970, and Chairman of the *8th International Symposium on the Chemistry of Natural Products* held at Delhi in 1972. He was President of the Indian Chemical Society, of the Indian Pharmaceutical Association and of the Oil Technologists Association of India. He was Chairman of the North Indian Section of the Royal Institute of Chemistry. He was President of the Indian Pharmaceutical Congress, General President of the Indian Science Congress (I966–67) and President of the Indian National Science Academy (formerly called the National Institute of Sciences of India) (1967–68). He was Vice-President of the Indian Academy of Sciences, Bangalore of which Sir C. V. Raman was the President. He received two medals from the Indian Chemical Society, the *Acharya Prafulla Chandra Ray Medal* and the *Acharya Jananendra Ghosh Medal,* and two medals from the Indian National Science Academy, the *Shanti Swarup Bhatnagar Medal* and *Meghnad Saha Medal.* He was one of the three Honorary Members of the Indian Science Congress Association elected on the occasion of its Silver Jubilee and he was an Honorary Fellow the Deutsche Akademie Naturforscher Leopaldina. He was Adviser to the London Chemical Society for India. In 1963, the President of India honoured him by conferring the title of *Padma Bhushan* for his distinguished services to science and public life in India.

Professor Seshadri had great affection for his students and helped them in all possible ways. He initiated them into research, guided them in their day-to-day research problems, helped them to write up research papers and theses, gave them training to express themselves lucidly before critical audiences, encouraged them to develop into capable leaders of science and even helped them financially whenever a need arose. He also helped them secure suitable positions in life. It was, therefore, not unusual that they celebrated his 60th, 65th, 70th and 75th birthdays and his election as Fellow of the Royal Society London (FRS) in a fitting manner. They raised funds and made endowments to the Andhra and Delhi Universities for instituting medals and prizes to mark his 60th birthday, and to the Indian National Science Academy to institute a medal to mark his 70th birthday. The first recipient of the Medal instituted in his name was Professor K. Venkataraman, a former Director of the National Chemical Laboratory, Poona and co-student of Professor Seshadri first at the Presidency College, Madras and later with Professor Robinson. On the occasion of the 60th and 75th birthdays, Professor Seshadri's students brought

out souvenirs and on the 65th and 70th birthdays they brought out two scientific publications. The 65th birthday volume was entitled, *Advancing Frontiers in the Chemistry of Natural Products* and contained nineteen reviews, contributed by his former students in their respective special areas; it was released and presented to him by Dr C. D. Deshmukh, then Vice-Chancellor of Delhi University. The 70th birthday volume entitled *Some Recent Developments in the Chemistry of Natural Products* and published by Prentice-Hall of India, contained sixteen articles contributed by eminent foreign scientists and nine articles contributed by Indian Chemists. The volume was released and presented to him by Professor D. S. Kothari, a former Chairman of the University Grants Commission.

Poignant Last Years

The last few years of Professor Seshadri's life make a sad reading. In the forties he had declined offers of positions of prestige and pelf, declaring that he would be only a University teacher. Later in 1960, he declined the offer of the Office of Chairman of the University Grants Commission. He had hoped that Chemistry would secure for him the resources to live a simple life. In 1965, he donated his personal library, the entire collection of books and journals of three decades, to the Delhi University Chemistry Department and continued to donate all the journals that he received subsequently also, hoping that he could work peacefully in the Department to the end of his life. In 1972, new rules and regulations of the Delhi University prevented him from receiving honoraria or remunerations from any quarters, thus bringing financial problems. They also came in the way of running research projects, thus cutting off all sources of research scholarships and funds for meeting research expenses. None could register with him for the Ph.D degree, and since in India no young graduate wants to do research unless he can get a Ph.D degree, all prospective students got diverted. He was without research grants and without means of subsistence. This was a great disappointment to him and affected him deeply, in spite of his moral courage and spiritual strength. In 1973, he had a second heart attack and in 1974, it was diagnosed he had gastric ulcer. A remarkable recovery followed and every thing looked bright till in September 1975 when it was discovered that something had gone seriously wrong. The gastric pain became acute and he vomitted blood repeatedly. The ulcer had turned malignant. He was rushed to hospital on the night of September 17. He was operated upon but his heart failed on the morning of September 27, 1975.

Thus ended the life of a great son of India who was rated by his compeers as one of the most eminent, most dedicated and most fearless among the scientists of the country, and a singular example of simplicity and humility. Professor Seshadri's passion for truth and rectitude was so great that he could never compromise on matters of profound importance for the welfare of society and the country. He never towed the path of worldly success by agreeing with others simply because they were powerful or belonged to influential, scientific or political groups. He was an unrelenting critic wherever things went wrong. The consequence was tragic and is best described by quoting from the 14th Founder Memorial Lecture (1978) of the Sri Ram Institute for Industrial Research, Delhi, delivered by Dr Atma Ram :

"Every scientist, however eminent, must be prepared to suffer the consequence of his individuality of opinions however scientifically correct they may be, if he does not fall in line with one or the other of the scientific groups or the political and bureaucratic power. We have in India the example of a scienist like T. R. Seshadri, who could not see eye to eye with the governmental scientific organisations in their manner of functioning, and was critical of the politician's interference and overlordship over scientific bodies, being singularly isolated to the extent that he had to undergo considerable suffering and die in penury."

Such was the poignancy felt by Dr Atma Ram and by many others over the neglect of this great scientist towards the end of his life. The author of the memoir came under the influence of Dr Seshadri in 1935, joined his research group in 1936, grew under him, looked upon him as his mentor, and, in a sort of rare and unconventional personal relationship, was a witness to all his glory and all his tragedies.

Professor Seshadri was survived by his wife and three daughters.

S. RANGASWAMI

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